Project Work Plan

Hanford 100-D Area Treatability Demonstration: Accelerated Bioremediation through Polylactate Injection

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1.0   Introduction

This work plan supports a new, integrated approach to accelerate cleanup of chromium in the Hanford 100 Areas. The current treatment approach was driven by a series of interim action of records of decision (RODs), issued in the mid-1990s (EPA 1996, 1999). The RODs were concerned primarily with protection of the Columbia River, by the means of reducing the mass of chromium in the groundwater. These RODs called for pumping groundwater and treating the extracted water with ion exchange technology and one innovative technology, the in situ redox manipulation (ISRM) barrier. The discovery of two new contaminated groundwater areas has resulted in the need to improve and accelerate the approach to groundwater clean up at the Hanford 100-D Area. This proposal is one component of an integrated strategy for accelerating remediation of 100-D Area groundwater. This new approach will provide supplemental treatment upgradient of the ISRM barrier by directly treating chromium and other oxidizing species in groundwater (i.e., nitrate and dissolved oxygen), thereby increasing the longevity of the ISRM barrier and protecting the ecological receptors and human health at the river boundary.

The new approach for the 100-D Area, shown in Figure 1, is summarized below:

- Immobilize chromium mass in the southwestern plume by injecting polylactate into the aquifer to stimulate bioreduction. A pilot-scale experiment at the 100-H Area, funded by the U.S. Department of Energy (DOE), has shown that the polylactate injection creates a persistent zone of chromium reduction that will continue to treat chromium under natural groundwater flow conditions.

- Mend the ISRM barrier by injecting micron-size zero-valent iron into areas that show signs of breakdown. Coupled with upgradient bioremediation, longevity of the ISRM barrier will be substantially increased, leading to a final ROD.

- Increase the pace of groundwater remediation by deploying an electrocoagulation treatment system, which is capable of treating high flow rates and high concentrations of chromium in an expanded pump-and-treat system. The existing ion exchange technology cannot support the more aggressive treatment scheme required to accelerate remediation, and will be decommissioned when the new system is in place. The initial system will be online in 2007. After expansion of this new technology, the existing system will be shut down by 2010.

- Find the chromium sources that feed the groundwater plumes in the 100-D Area. This information will be used to remediate the sources, which will also accelerate cleanup and lead to a final ROD.

- Remediate waste sites along the Columbia River by 2012 through the River Corridor contractor.

- Continue to prevent future groundwater contamination by reducing artificial recharge, e.g., remove or repair leaking water lines.

In this integrated approach to chromium cleanup, three innovative technologies will be deployed in the 100-HR-3 Operable Unit. This approach is estimated to reduce life-cycle costs in excess of $40M and significantly accelerate chromium cleanup in the 100 Areas.
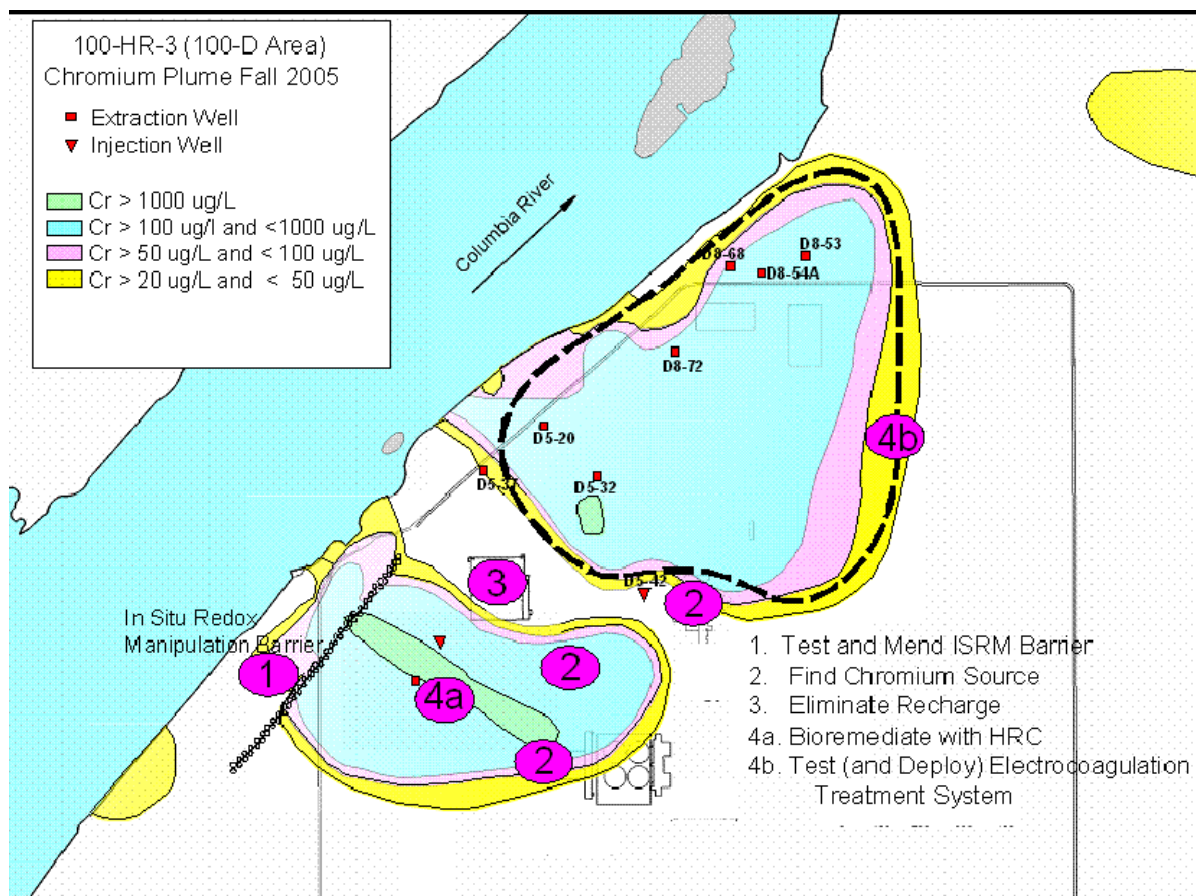
Figure 1. Components of System Approach to Groundwater Remediation in the 100-D Area (The polylactate treatability test will be performed in the vicinity of 4a.) (Adapted from FHI 2006.)

This work plan supports the accelerated cleanup (under the first bullet above) by performing a field-scale treatability test for bioreduction of chromate. In addition to remediating a portion of the plume, the data from this test will be valuable for designing a full-scale bioremediation system to apply at this and other chromium plumes at Hanford.

2.0   Technology Description

2.1   Background

Limited field investigations and a qualitative risk assessment performed in the 100-HR-3 Operable Unit have established that hexavalent chromium is a groundwater contaminant of concern for ecological receptors in the Columbia River. An interim action ROD (DOE 1999) was issued for the 100-HR-3 groundwater Operable Unit in 1996 to address the chromium plume that was entering the Columbia River in the 100-D (Figure 1) and 100-H Areas at levels exceeding the ambient water quality level of 10 ppb. The preferred alternative action in the interim action ROD was pump-and-treat technology, using ion exchange columns as the treatment technology. The 100-D Area aquifer has the highest concentrations of

chromium on the Hanford Site (> 2000 ppb). Samples from aquifer tubes located near the river shore contain chromium concentrations at levels greater than 200 ppb (>20 times the aquatic standard, and >10 times the Remedial Action Objective of 20 ppb).

Chromium at varying concentrations was introduced to the soil and groundwater in the 100 Areas from a number of sources. The largest plumes were caused by disposing reactor coolant to surface basins. This coolant (with an initial maximum chromium concentration of about 700 ug/L) was treated with sodium dichromate to inhibit corrosion in the reactor cooling system. After passing through the reactor, the coolant flowed through large-diameter underground pipes to retention basins for thermal and radioactive cooling prior to discharge to the Columbia River. When fuel cladding ruptures occurred, trenches and cribs were used to dispose of the radiologically contaminated cooling water. Cooling system piping and retention basins leaked large volumes to the ground, creating substantial groundwater mounds and raising the water table over large portions of each reactor area. For example, the groundwater mound in the 100-D Area was 10 to 20 ft higher than the ambient water table. These mounds dissipated following cessation of reactor operations.

Higher concentrations of chromium (>700 ug/L) were also introduced to the soil and migrated downward to groundwater through relatively localized areas. Leaks and spills of concentrated sodium dichromate stock solutions likely occurred where it was stored and handled. Chromic acid was used to decontaminate reactor equipment and was then disposed to french drains, cribs, and trenches.

In addition to the 100-D chromium plumes, oxidizing species, such as nitrate and dissolved oxygen (DO), have a significant impact on ISRM barrier longevity. Groundwater nitrate concentrations upgradient of the ISRM barrier are about 60 mg/L over a wide spread area (Figure 2). DO is currently being monitored in the wells up- and downgradient of the ISRM barrier. Monitoring data show that DO in upgradient wells were near saturation levels, ranging from 6.11 to 9.53 mg/L. DO concentrations from wells within the treatment barrier show the effects of a strong reducing environment, ranging from 0.10 to 3.00 mg/L. DO concentrations in compliance wells downgradient of the barrier ranged from 1.76 to 6.22 mg/L immediately down gradient of the treatment zone, while DO concentrations in two wells located slightly beyond the limits of the treatment zone ranged from 6.39 to 7.77 µg/L. These data show that dissolved oxygen in groundwater entering the ISRM barrier will have a significant Impact on barrier longevity and that DO is replenished in groundwater as it travels downgradient of the barrier. It follows that any remedial approach that reduces dissolve oxygen concentration upgradient of the ISRM barrier will increase barrier longevity.

2.2 Chromium(VI) Immobilization Using Lactate/Polylactate In Situ Biostimulation

Enhancing anaerobic bioremediation is based on using lactic acid (formula $CH_3 CH(OH) CO_2 Na$ as aqueous solution). Environmentally safe, food quality polylactate ester releases lactic acid upon hydration (Sharma et al. 2001), which provide a carbon and energy source, stimulating both aerobic and anaerobic microbes. Anaerobic microbes ferment the lactic acid into pyruvic acid and then to acetic acid (Gibson and Sewell 1992), releasing 2 moles of molecular hydrogen per mole of lactate. Since hydrogen
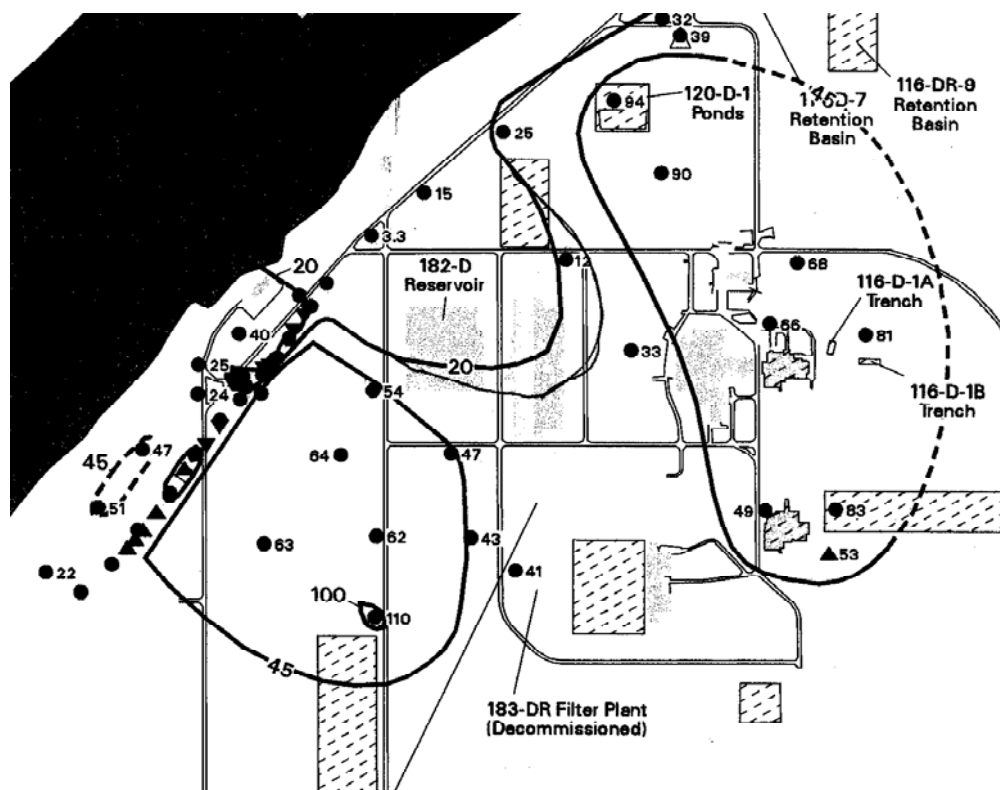
Figure 2.   Hanford 100D Area Ground Water Nitrate Concentrations in 2004 (the ISRM barrier is in the left center.)

gives up an electron easily, it is a primary electron donor for microbes that reduce electron acceptors, such as oxygen, nitrate, iron, sulfate, and chlorinated hydrocarbons (Hemond and Fechner 1994). When applied to chromium contaminated aquifers, polylactate stimulates the microbial community to generate the reductant H, and also can abiotically reduce Cr(VI) to Cr(III), which rapidly precipitates (HRC 2001). Polylactate and its breakdown products accelerate the reduction process and cause the microbial population to remove the oxygen, nitrate, sulfate and other competing electron acceptors, which, in turn, depress the redox potential in the aquifer down to the appropriate low values needed for the transformation of Cr(VI) species to Cr(III) species that are precipitated on soil particle surfaces. Investigations with the polylactate compound (HRC 2001) showed that reducing conditions could last for up to 18 months with a single polylactate application. The ongoing pilot test of Cr(VI) biostimulation at Hanford 100-H Area, which started in 2004, shows that the total chromium concentration in the monitoring well decreased by a factor of 4 compared to that under background conditions. Specifically, one month after polylactate amendment, Cr(VI) values fell below ~20 ppb with one exception of 22 ppb. Values after injection of the amendment averaged ~12 ppb. The Cr(VI) concentration in the monitoring and pumping wells remained below background concentrations and the Remedial Action Objective of 20 ppb even after 1.5 years, when redox conditions and microbial densities had returned to background levels. This renders a cost effective aquifer treatment as compared to other remediation technologies (Bryant 2001).

2.3 Nitrate Reduction Using Lactate/Polylactate In Situ Biostimulation

Hydrogen release compoung (HRC) was cited by the manufacturer in two field case studies for use in the reduction of nitrate contamination of groundwater (www.regenesis.com). HRC was used at a Department of Defense (DOD) site for remediation of explosives and nitrate and a second site was an agricultural facility with nitrate contamination from fertilizer. Groundwater contamination at both these sites was relatively shallow (~35 ft) and the HRC was emplaced through an array of injection points. At the DOD site, nitrate concentrations were reduced from 52 to 94 percent 105 days after injection. A 99 percent reduction in nitrate concentrations in monitoring wells was reported at the agricultural site about 1 year after HRC injection (pretest nitrate concentrations ranged from 30 to 65 mg/L with post treatment concentrations at 0.3 mg/L).

2.4 Polylactate Technology Implementation

The polylactate compound is manufactured as a dense (density of 1.3 g/cm^3) and viscous gel (viscosity of approximately 20,000 centipose), containing both slow and fast releasing polylactate esters. The slow releasing compound is bound in a high viscosity polymer that releases the lactic acid slowly. The fast releasing compound is bound in a low viscous polymer that releases the lactic acid more quickly (up to one order of magnitude faster than the slow release compound) and can affect a larger volume of water. Indigenous anaerobic microorganisms ferment lactic acid or lactate to produce hydrogen (H_2) that is a required electron donor for reducing Cr(VI), dissolved in groundwater, to Cr(III) that is then precipitated onto sediment particles. Polylactate should be heated (to at least 105°F) prior to injection. Polylactate is usually injected into the aquifer, as an emulsion of polylactate and water to decrease viscosity, using direct-push technologies or through specially designed injection wells.

The radius of influence of polylactate mostly depends on lithology of a water-bearing formation, groundwater velocity, and the amount of polylactate injected through the borehole. After the injection, polylactate's radius of influence in groundwater depends on advection (groundwater velocity) and chemical diffusion processes. The presence of polylactate and its byproducts in an aquifer can be determined using both qualitative and quantitative methods, including the determination of DO and oxidation-reduction potential (ORP). Polylactate causes highly reducing conditions with the DO concentration at or near zero and the ORP of zero or negative. Detecting polylactate in an aquifer also involves the determination of the total organic carbon (TOC) and metabolic acids, including acetic, butyric, lactic, propionic, and pyruvic acids. The TOC test simply measures the levels of carbon present in a groundwater sample (aquifer). Because polylactate is a high molecular weight carbon source, its injection into an aquifer will increase the overall mass and concentration of TOC.

The frequency of applying polylactate varies from site-to-site and is dependent on the site's application strategy and goals. There are two polylactate application approaches: grid- and barrier-based. A grid-based polylactate approach is used to treat an entire groundwater plume, and a barrier-based approach is used to cut-off the plume migration through the groundwater. The frequency and quantity of polylactate application is dependent on the presence of the contaminant source, groundwater velocity, and aquifer/sediments biogeochemistry. According to past investigations conducted with polylactate, it has a field longevity of 12-18 months.

2.5   Need for Supplemental Treatment upgradient of the ISRM Barrier

Although the primary purpose of the ISRM barrier was to immediately protect the Columbia River, additional remediation is required to address the high concentration portion of the chromium plume behind the ISRM barrier and to increase the longevity of the barrier, portions of which have been exhibiting signs of premature breakdown. The proposed method to accomplish this is to introduce polylactate into the aquifer to biologically reduce hexavalent chromium and other oxidizing species (i.e., nitrate and DO) and establish a permeable reactive barrier that will continue to treat chromium and nitrate under natural groundwater flow conditions.

It is clear from monitoring data that the chromium plume is being fed by a continuing source of hexavalent chromium. Locating and remediating this source is a high priority task for the Groundwater Remediation Project, but even after source remediation the 700-m-long plume will continue to be a threat to the river. Current modeling predicts it will take at least 40 years for the plume with concentrations > 20 ppb to move through the ISRM barrier, which is well in excess of the 20-year design life of the barrier.

2.6   Alternative Technologies Considered

The principal alternative technology considered was calcium polysulfide injection, which creates reducing conditions and results in the reduction of Cr(VI) to Cr(III). A primary concern associated with use of polysulfide is that the treatment would not be compatible with the use of the zero-valent iron treatment planned as part of the overall remediation scheme. Current plans are to inject zero-valent iron into several of the failing ISRM barrier wells. Another issue is the potential to adversely affect the aquifer and river by changing the groundwater chemistry. Among these are DO, oxidation-reduction potential, pH, iron, manganese, lead, and arsenic. The listed metals, which are naturally present in the aquifer materials, typically are mobilized in a reducing environment but quickly re-precipitate when they reach an oxic environment.

Polylactate is expected to be less harsh and have a lower probability of geochemical impact while still achieving the desired goal of eliminating the high concentrations of chromate, nitrate, and dissolved oxygen upgradient of the ISRM barrier. Bioremediation using polylactate is also likely to be sustained over longer time periods via the slow release of polylactate and buildup of biomass. Polylactate is, therefore, the preferred alternative.

Use of pump-and-treat technology is another potential alternative to be considered. However, because the southwest chromium plume is already being treated passively by the ISRM, the use of this technology could be considered counter-productive because it could lead to reduction in the overall effectiveness and longevity of the ISRM barrier if not carefully designed. Studies have also generally shown that use of permeable reactive barriers have lower life-cycle costs than pump-and-treat systems.

3.0   Project Scope

The overall scope of the project is to bioreduce Cr(VI) to Cr(III), thus removing chromate from groundwater in a portion of the 100-D Area plume upgradient from the ISRM barrier. Field-scale treatability testing of polylactate stimulated bioreduction of chromium in the 100-D Area is divided into 5 tasks as follows: (1) Project Management, (2) Development of a Conceptual Model and Preliminary

Analysis of Polylactate Injection, (3) Pilot Scale Treatability Test, (4) Performance Assessment Monitoring, and (5) Data Analysis and Reporting. Each task is described in the following sections. Key outcomes of each task will be carefully tracked. Selected tasks include go or no-go decision points that help ensure that the project will result in the technically feasible cleanup technology and deployment approach for the treatment of chromium and nitrate in groundwater. This project will provide key field-scale treatability data that will support design of a proposed layout of additional wells needed to fully treat the 100-D Area plume up gradient from the ISRM barrier, and a plan for monitoring the system biogeochemically and geophysically to provide the desired assurance of effective treatment at minimum cost.

3.1   Task 1: Project Management

Subtask 1a – Project Support. Plan, organize, and provide top-level guidance and direction for overall project performance. Also provide project-level cost and schedule control, tracking, and reporting. Coordinate the Columbia River Protection Supplemental Technologies Project work scope with DOE, Richland Operations, the Groundwater Remediation and Closure Assessment Project and the Office of River Protection, including participation in planning, peer reviews, and periodic project meetings.

Subtask 1b – Planning and Test Plan Preparation. This work element consists of developing both a laboratory-scale experimental approach and a field-scale treatability testing approach, and preparing planning documents. An experimental plan will be prepared at the beginning of the project to cover bench-scale laboratory testing. Once preliminary bench-scale testing results and site-specific characterization data are available, a field test plan will be prepared. Each plan will provide a description of planned testing activities, sampling and analysis methodologies, and data quality requirements.

Subtask 1c – Work Order to Fluor Hanford, Inc. Fluor Hanford, Inc. will review the treatability test plan and report; coordinate with other site contractors; provide operations site and representative support, regulatory, rad con and health and safety support; and assist in project coordination.

3.2   Task 2: Development of a Conceptual Model and Preliminary Analysis of Polylactate Injection

This work element will include three subtasks: (1) development of a conceptual model and evaluation of hydrogeological and biogeochemical conditions of the Ringold formation, (2) evaluation of polylactate injection approaches and design of a well network to support treatability testing, and (3) prediction of polylactate distribution and treatment efficiency.

Subtask 2.1 – Development of a Conceptual Model of Hydrogeological and Biogeochemical Conditions. This subtask will involve the evaluation of hydrogeological and biogeochemical conditions from existing wells and boreholes in the vicinity of the proposed treatability test site (Figure 3) and incorporating this information into a working conceptual model of the site.

Subtask 2.2 – Evaluation of Polylactate Injection Approaches. The objective of this subtask is to develop a preliminary treatability test design (general operation and well layout) for the emplacement based on currently available site characterization data. This task will also develop the tools to be used in

the final test design once site-specific characterization data becomes available. This task will include three subtasks: (1) quantify biogeochemical processes, (2) evaluate multi-fluid flow aspects of injection
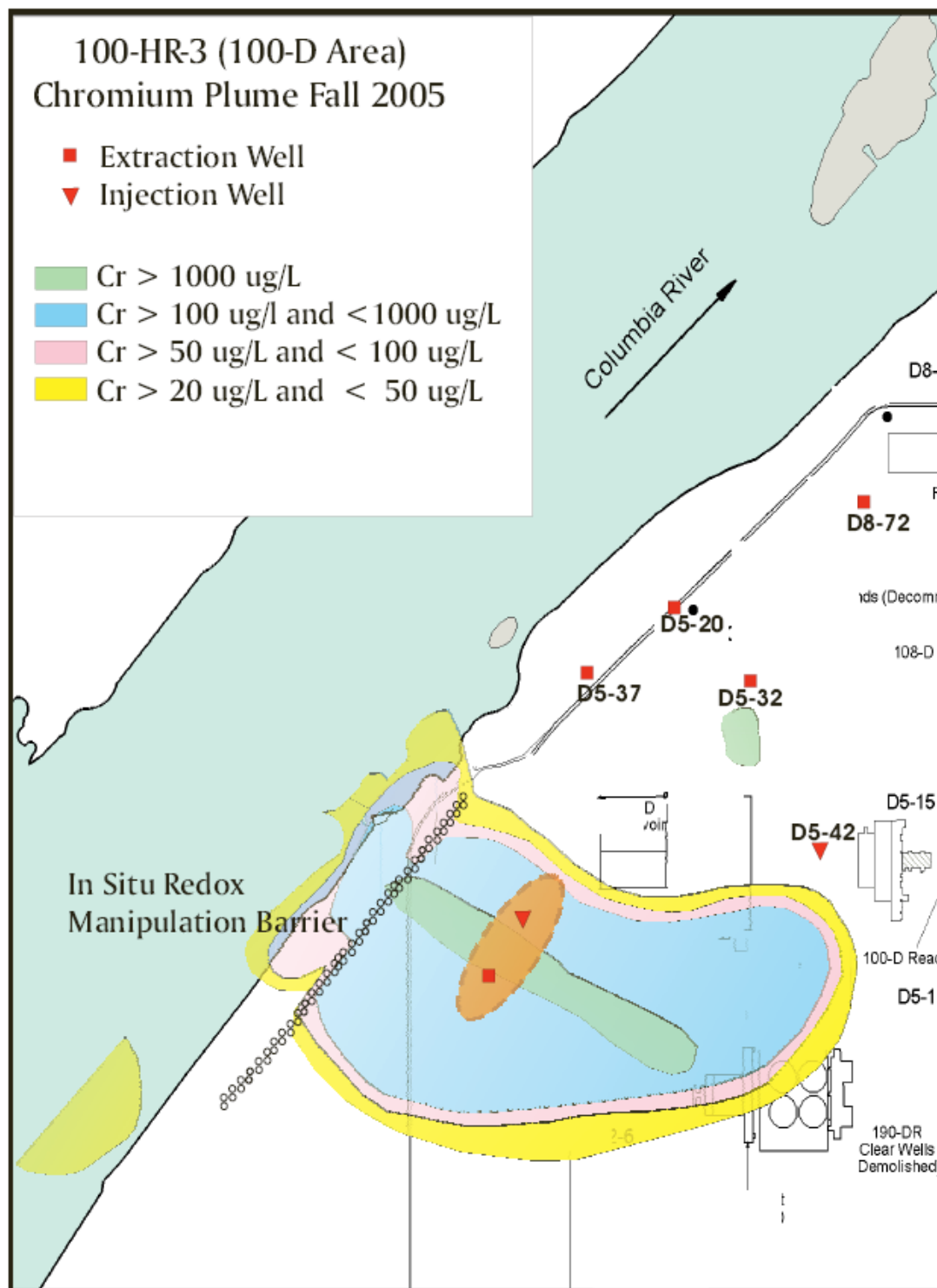

Figure 3. Location of Existing Wells in 100-D Area

of dilute polylactate emulsion and determine whether sufficient data are available to support injection design analysis, and (3) develop initial test design and site well layout (e.g., dipole or other potential injection approaches).

Subtask 2.3 – Prediction of Polylactate Distribution and Treatment Efficiency. Based on the site conceptual model and the injection design analysis performed in the previous two subtasks, this subtask will involve making preliminary predictions of the polylactate distribution and treatment efficiency of the injection approach selected. The selected pilot field test design will be evaluated in this subtask with the goals of (1) providing the field scale information needed to develop a full scale remedial design, (2) maximizing the distances over which polylactate can be distributed, (3) minimizing the number of wells, and (4) optimizing the effectiveness of treatment and removal of Cr(VI) from groundwater. In addition to the dipole injection approach used during the EM-50 field experiment at 100-H Area, the effectiveness of single well radial injections will be evaluated to determine which approach would be most effective under the complex hydrogeologic conditions of the 100D Area site.

3.3   Task 3: Pilot-Scale Treatability Test

This work element includes installation of a test site well network and associated site-specific characterization, injection design analysis, test systems design and setup, and the pilot scale field test. The injection design analysis will incorporate results from the laboratory experimentation and available site characterization data. Additional wells installed by this project will be used for operational and performance monitoring purposes.

Subtask 3.1 – Collection of Site Specific Characterization Data. Data collected during well drilling will be used to refine the hydrogeologic and geochemical conceptual model and select the most appropriate injection approach for a field-scale demonstration of polylactate treatment. Data collected during this investigation will include geologic logging and depth discrete characterization of the sediment's physical, biogeochemical, and hydraulic properties. It is anticipated that one or two injection/extraction wells and up to five monitoring wells will need to be installed to support the deployment and monitoring of the polylactate injection test. The final number and locations of wells will be determined based on results from Task 2 and the availability of funding.

Following installation of the monitoring well network, several hydrogeologic characterization methods will be used to obtain additional site specific information. These tests include hydraulic testing to obtain formation hydraulic properties, electromagnetic borehole flowmeter (EBF) testing to assess the vertical distribution of horizontal hydraulic conductivity (i.e., vertical heterogeneities), and a conservative tracer injection test. The tracer test will be used to further evaluate formation heterogeneities, to assess the downgradient transport of the tracer plume (i.e., aquifer transport properties), to refine the polylactate injection design, and test operational procedures.

Subtask 3.2 – Bench-scale Microbiological Experiments. Sediment samples collected during well installation will be tested for response to biostimulation by polylactate. The basis for this testing is to assure that Ringold Formation gravels are similar in biostimulation response to the Hanford formation near 100-H Area. Standard bottle incubation will be performed. Required response will be at least 33% of the activity and biomass as was obtained for similar samples from the Hanford formation. Results of this testing represent a go, no-go step for the project.

Subtask 3.3 – Evaluation of Column-Scale Experiments of Geochemical Effects of Polylactate.
Experiments related to evaluating the geochemical impact of the polylactate in its deployed form in
Ringold sediments will be performed. Lawrence Berkley National Laboratory (LBNL) is currently
performing experiments on Hanford formation sediments as part of another project and those results will
be evaluated to determine if additional experiments are needed on Ringold sediments. It is likely that
existing information will be adequate. However, this is an important decision point, since additional
column experiments could have a cost and schedule impact (see Subtask 3.4 and Section 4.0).

Subtask 3.4 – Evaluation of Multiphase Flow Dynamics. The objective of this task will be to evaluate
the multi-fluid flow aspects associated with the injection of a dilute polylactate emulsion. This task will
include measurements of fluid properties (e.g., density, viscosity) of different formulations and dilutions
of polylactate. It will also include column studies of these different polylactate formulations to measure
concentration and distance traveled under a range of field-scale injection rates. A dual-gamma system
will evaluated for suitability for collecting insitu-measurement of the polylactate solution in the column
tests. The columns will also be equipped with sampling ports for collecting measurements at different
distances from the inlet. The results of these experiments will be used to help determine the multi-fluid
flow parameters for the simulations used in the field test design (Task 2, Section 3.2).

Subtask 3.5 – Injection Design Analysis. Models developed in Task 2 will be updated with results of site
characterization data and laboratory experiments to develop the final test design. The design will include
overall test operation, injection/pumping rates, volumes, and duration. This design tool will incorporate
both bench-scale experimental results and site-specific characterization data and will be used to evaluate
the various geohydrologic, geochemical, and polylactate reaction mechanisms that control emplacement
of a polylactate amended treatment zone. The model will be used to design both the tracer and
polylactate injection strategies.

A sampling and analysis plan for the injection and for long term monitoring will also be developed based
on the results of these simulations.

Subtask 3.6 - Polylactate Injection at Selected Pilot Test Site Location. Based on results from Subtasks
3.1 through 3.3 and results of drilling at the test site, a pilot-scale field test of the technology will be
conducted at the selected location. Operational parameters (volumes, rates, concentrations),
constituents/field parameters monitored and sampling frequency will be determined based on the
implementation approach selected and the scale of the field treatment. Monitoring data collected during
the polylactate injection test will be used to assess the areal extent of treatment and, along with the
injection design analysis results, be used to determine an appropriate temporal and spatial sampling
distribution for assessing technology performance.

3.4   Task 4: Performance Assessment Monitoring

Groundwater samples will be collected and analyzed to evaluate treatment performance. Hydraulic tests
will be conducted following emplacement of the treatment zone and compared with pre-treatments values
to assess the impact of treatment on aquifer hydraulic properties.

Subtask 4.1 – Groundwater Analyses. Inductively coupled plasma – mass spectrometry (ICP-MS),
inductively coupled plasma – optical emission spectrometry (ICP-OES), and ion chromatography (IC)
will be used to quantify aqueous cation, anion, and trace metal concentrations, respectively. Data will be

collected before, during, and following deployment of the polylactate amendment. This will allow changes in aqueous concentrations, and speciation, due to amendment implementation to be tracked and correlated with the formation of solid phases within the sediment.

Subtask 4.2 – Post-treatment Hydraulic Testing. Hydraulic tests will be conducted following emplacement of the treatment zone and compared with pre-treatments values to assess the impact of treatment on aquifer hydraulic properties. Specifically, pre- and post-treatment hydraulic responses will be compared to determine whether any degree of aquifer plugging occurred.

3.5 Task 5: Data Analysis and Reporting

This work element consists of managing, compiling, and evaluating all of the data generated during the treatability studies and preparing a treatability test report. The final report will cover activities ranging from basic laboratory development work through a field scale demonstration of the technology. Findings presented in this report will form the basis of an evaluation of this technology for full scale implementation.

4.0   Assumptions

The following assumptions pertain to this scope of work:

- The project will start on or before June 15, 2006.

- A project specific Quality Assurance Plan (QAP) is required. This will describe the type of experiments, chemical and microbial analysis, and the associated detection limits, duplicates, blind duplicates, and other quality assurance information.

- This treatability study will focus on chromium immobilization by bioreduction in the saturated zone and will not address treatment of possible chromium sources in vadose zone porous media.

- The schedule shown in this proposal will be approved by DOE and the appropriate regulatory agencies.

- Fluor Hanford, Inc. will be able to provide drilling services for the project according to the proposed schedule.

- Investigation derived waste disposal services will be provided by Fluor Hanford, Inc.

- Ongoing or existing column experiments with HRC and Hanford sediments will be adequate to support field test design.

5.0   Schedule

A detailed schedule for the polylactate treatability test is shown in Table 1.

6.0   Budget

The total budget for this plan is estimated to be approximately $1,507,451.

Table 1. Schedule for the Polylactate Treatability Test

Schedule for 100 D Area Polylactate Treatability Study	←—— FY 06 ——→							←———————— FY 07 ————————→												←———————— FY 08 ————————→								
	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Task 1.0: Project Management																												
Project management			▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
Task 2.0: Development of Conceptual Model and Preliminary Analysis of Polylactate Injection																												
Conceptual model development and modeling design analysis				▓	▓	▓	▓	▓																				
Task 3.0: Pilot-Scale Treatability Test																												
Well Installation (planning and installation)					Planning			Install																				
Test systems design, procurement, mobilization, setup					▓	▓	▓	▓	▓	▓	▓	▓	▓															
Bench scale microbial experimentation								▓	▓	▓	▓																	
Column Studies of Mulit-phase effects of Polylactate				▓	▓	▓	▓	▓	▓	▓	▓	▓																
Injection Design Analysis								▓	▓	▓	▓	▓																
Hydraulic and Tracer injection testing										▓	▓																	
Field Test Plan Preparation							▓	▓	▓	▓	▓	▓																
Geophysical Characterization Pre/Post injection test											▓						▓											
Polylactate injection test														▓														
Task 4: Performance Assessment Monitoring																												
Post-injection aqueous sampling and analysis																	▓	▓	▓	▓	▓	▓	▓					
Analytical costs																	▓	▓	▓	▓	▓	▓	▓					
Task 5.0: Data Analysis and Reporting																												
Data Analysis																	▓	▓	▓	▓	▓	▓	▓	▓	▓			
Reporting																										▓	▓	▓

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7.0 References

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Appendix A

Scientific Basis for Proposed Field Test

Appendix A

Scientific Basis for Proposed Field Test

A.1   Chromium Contamination in Subsurface at 100 D and ISRM

According to the recent annual groundwater monitoring report for FY 2005 (Hartman et al. 2006), chromium contamination underlies most of the 100-D Area in two plumes (Figures A.1 and A.2). The north plume had sources in the central 100-D Area and the south plume had unknown sources near the former 183-DR filter plant. The area devoid of chromium contamination between the two plumes is likely related to leakage of clean water from the 182-D reservoir

Aquifer tubes provide additional monitoring points along the 100-D Area shoreline (Figure A.3). Historically, the highest concentrations were downgradient of the south chromium plume. The highest concentration in fiscal year (FY) 2005 was in the central 100-D Area shoreline.

North Plume. The axis of the north chromium plume extends from the former reactor building toward the northwest, perpendicular to the Columbia River. Near the former sources, chromium continued a gradual decline in most wells (e.g., well 199-D5-16 in Figure A.4. Well 199-D5-15 is an exception to this declining trend; the average concentration in August 2005 was 1,066 µg/L, the highest value in this well since 1994. Chromium concentrations in well 199-D5-15 have been variable since FY 1997. Until 2003, specific conductance and other constituents varied with the chromium, suggesting dilution of groundwater with fresh water. Specific conductance stabilized in 2003 at ~600 µS/cm. Chromium continues to fluctuate, but not as widely as it did from 1999 to 2002.

In the north 100-D Area near the pump-and-treat system, compliance wells continued to show variable chromium concentrations, with the lowest concentrations in the early summer when river stage was high (Figure A.5). The concentrations remained above the remedial action goal in the compliance wells except for a few samples collected in early summer. The seasonal concentration peaks (fall and winter of each year) have declined since 2000.

On the southwest side of the north plume, chromium concentrations in wells 199-D5-20 and 199-D5-41 decreased from their peak values observed in 2004. Chromium concentrations dropped from 1,400 µg/L in May 2004 to 622 µg/L in May 2005. In well 199-D5-41, concentrations dropped from 2,500 µg/L in November 2004 to 1,550 µg/L in May 2005. The cause of the variable concentrations in this part of the plume is unknown.

Chromium concentrations in aquifer tubes in the north 100-D Area are consistent with concentrations in the aquifer. The highest concentration was 518 µg/L at tube site AT-36.

South Plume. This chromium plume lies south and southwest of the 182-D reservoir and west of the 183-DR filter plant, extending to the Columbia River (see Figures A.1and A.2). The core of the plume, with concentrations >500 µg/L, is oriented southeast-northwest, perpendicular to the Columbia River. The ISRM barrier intersects the south chromium plume and terminates the highest-concentration portion of the plume.

Chromium concentrations in the south plume have varied by an order of magnitude in some wells since 2001, and the reason for the variability is not understood. The source of this plume has not been located despite previous investigations (e.g., Thornton et al. 2001). DOE is continuing to characterize the site in an attempt to identify the source or sources of chromium contamination.

Compliance monitoring wells down gradient of the ISRM barrier show inconsistent trends. The northernmost well, 199-D4-83, shows variable chromium concentrations with decreasing peaks. Well 199-D4-39, near the north end of the barrier, shows high variability since 2000, with concentrations over 850 µg/L during FY 2005. South of well 199-D4-39, chromium trends in wells 199-D4-23, 199-D4-84, 199-D4-85, and 199-D4-86 continued to decline overall, with some variability. Concentrations in well 199-D4-38 have shown an increasing trend in FY 2004 and 2005. Concentrations in the southernmost wells, 199-D4-85 and 199-D4-86, were below the remedial action goal (20 µg/L) for much of the fiscal year.

The highest concentration in an aquifer tube in the south chromium plume was 233 µg/L at tube site Redox-3. Chromium concentrations in several of the tubes in this region have declined since they were first sampled in 1997. The decline may be caused, in part, by remediation effects.
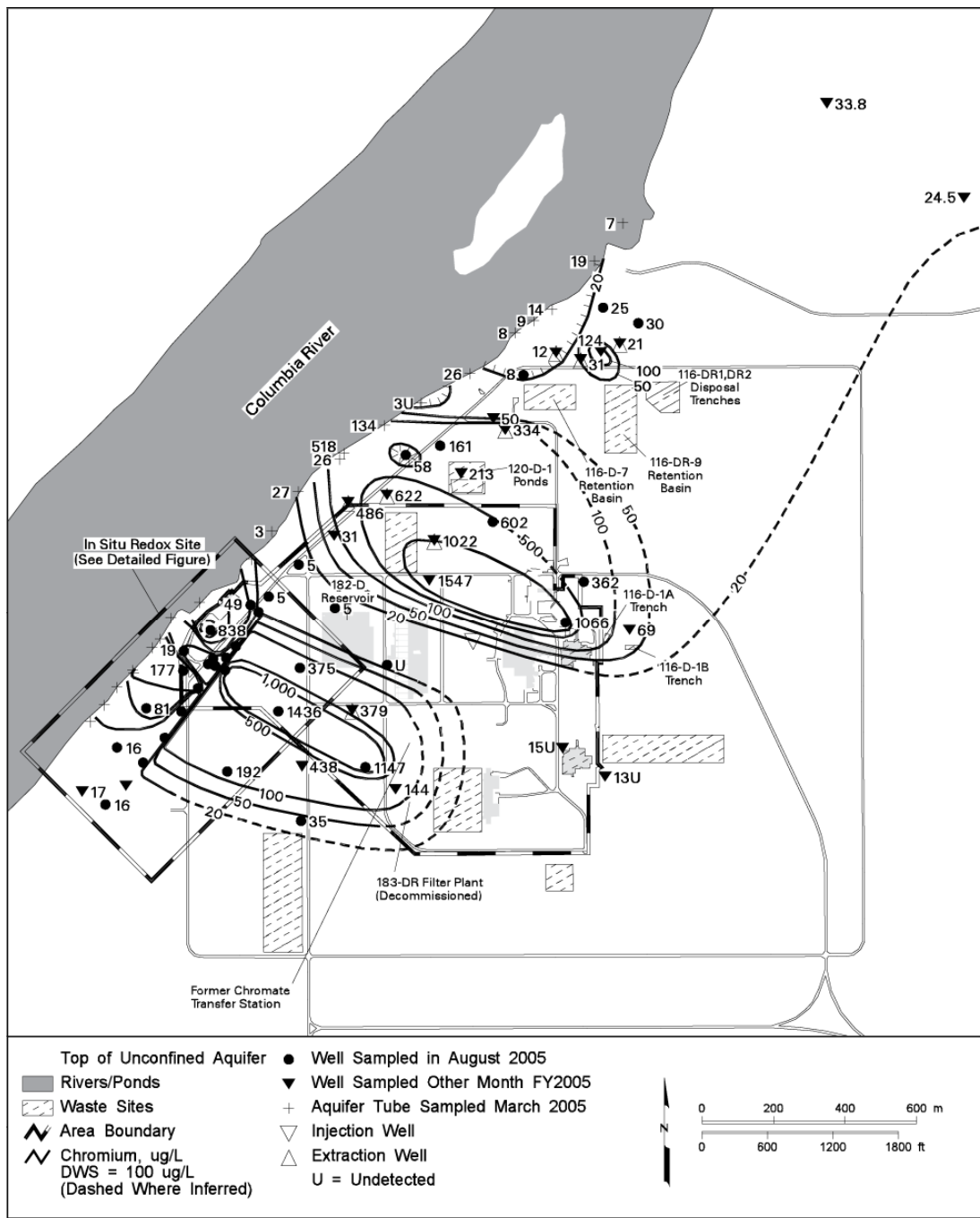
Figure A.1. Dissolved Chromium Concentrations in the 100-D Area, Top of Unconfined Aquifer, August- September 2005
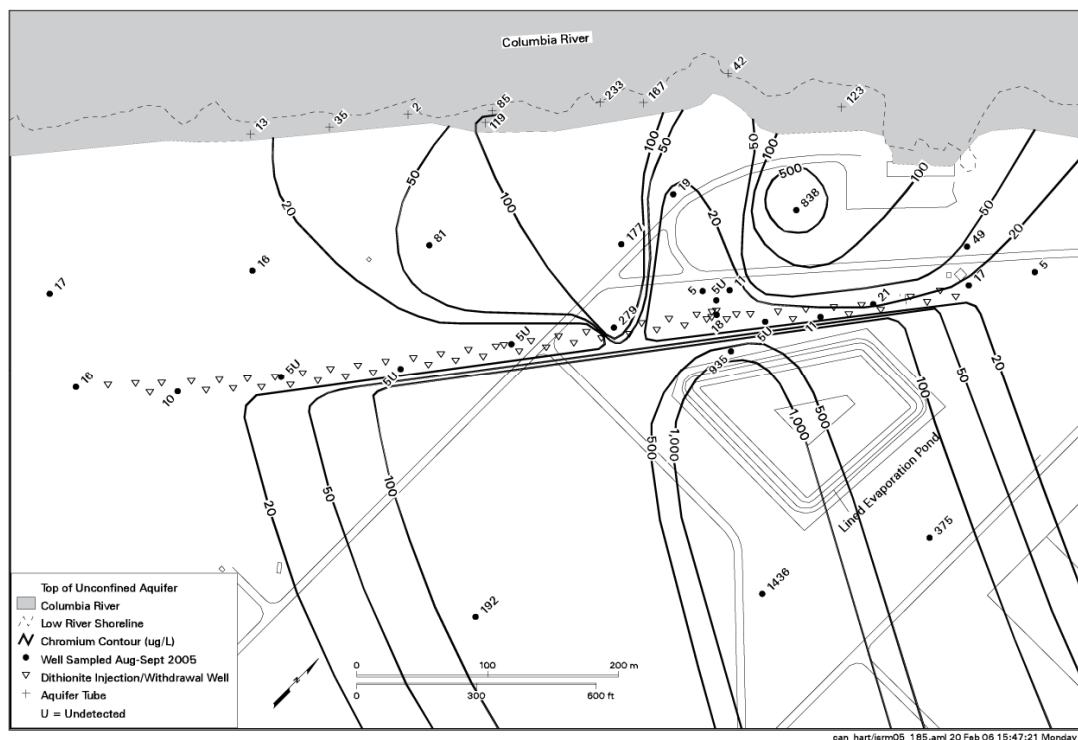
Figure A.2. Dissolved Chromium Concentrations Near the ISRM Site, 100-D Area, August 2005
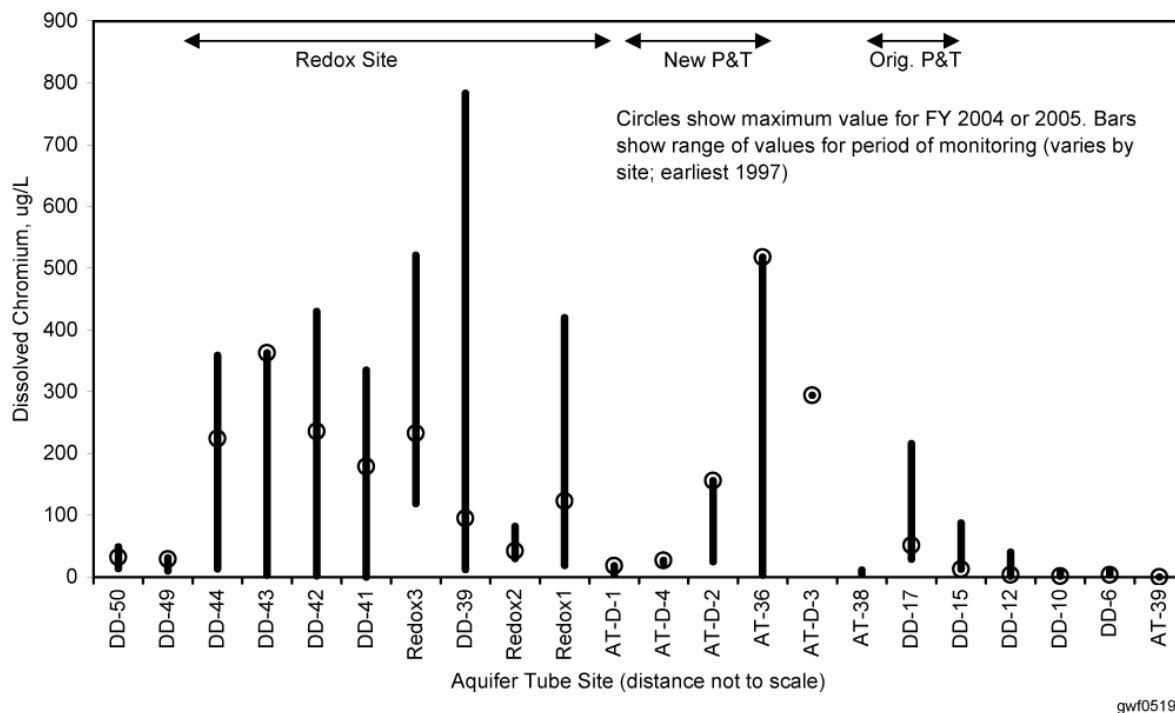

Figure A.3. Dissolved Chromium Concentrations at Selected Aquifer Tube Sites at 100-D Area

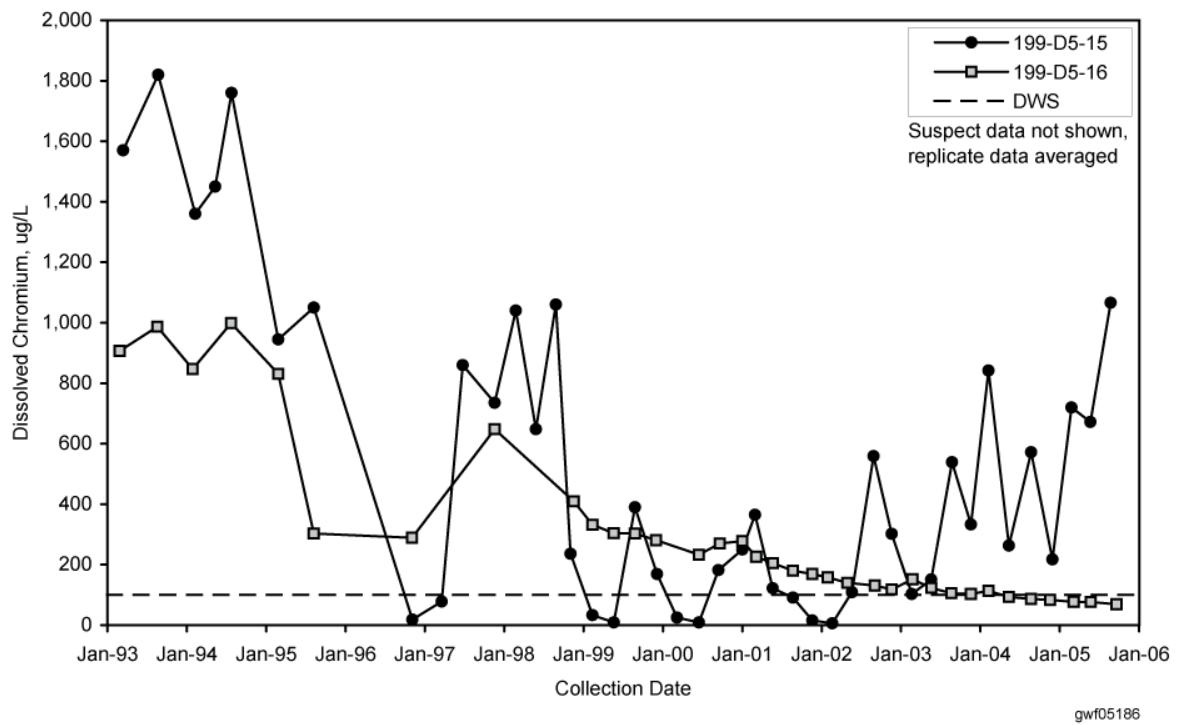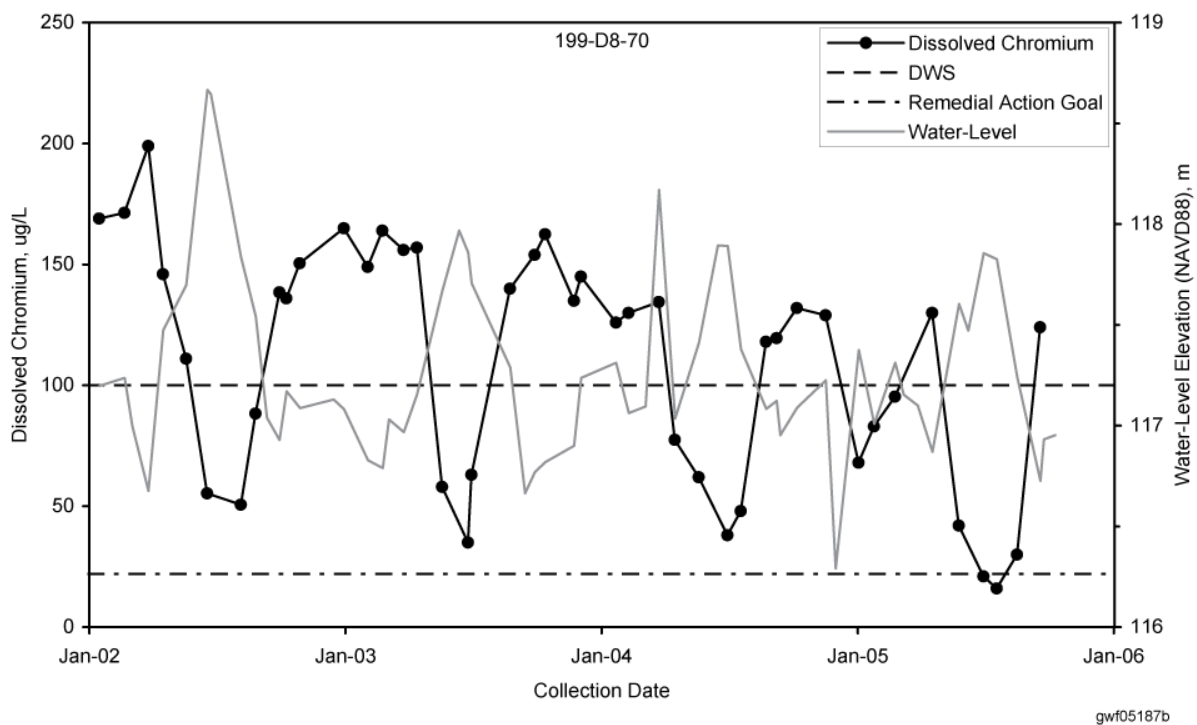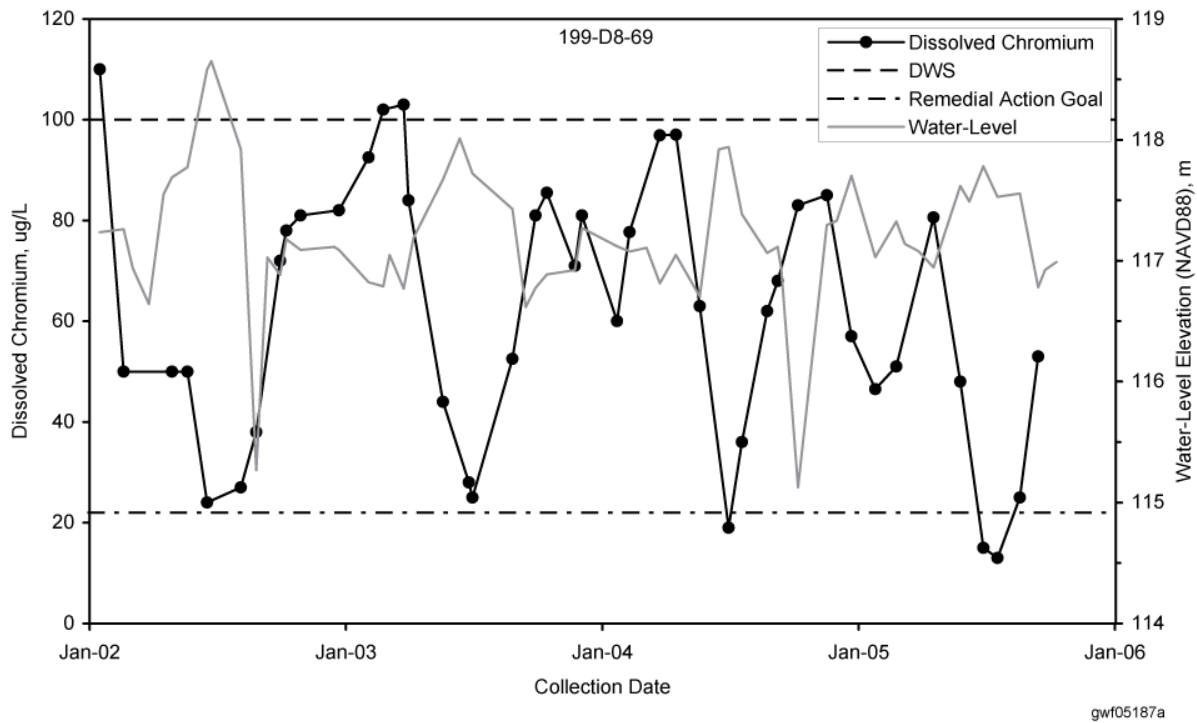**Figure A.4**. Chromium Concentrations in Wells Near Former D Reactor

gwf05187a

gwf05187b

gwf05187

Figure A.5. Dissolved Chromium Concentrations and Water Levels in Compliance Wells for the 100-HR-3 Pump-and-Treat System at 100-D Area

A.6

A.2   Chromium Immobilization by Bioreduction of Cr(VI) to Cr(III)

A number of abiotic reactions may be responsible for the transformation of dissolved Cr(VI) into immobile Cr(III) that precipitates onto sediment particles. For example, in soil solutions, Fe(II), S(-II), and various organic compounds including fulvic and humic acids, have been shown to reduce Cr(VI) (Eary and Rai 1988; Pettine et al. 1998; Elovitz and Fish 1994; Wittbrodt and Palmer 1995, 1996). Reduction of Cr(VI) on surfaces of Fe(II) solids (biotite, Fe(II) impurities in   -FeOOH, FeS, magnetite, ilmenite, green rusts) has been extensively investigated (Bidoglio et al. 1993; Anderson et al. 1994; Ilton and Veblen 1994; White and Peterson 1996; Loyaux-Lawniczak et al. 2000).

Common soil minerals such as TiO2, Al2O3, FeOOH, montmorillonite, and kaolinite have been shown to catalyze Cr(VI) redox reactions with organic compounds and Fe(II) (Deng, and Stone, 1996a,b; Buerge and Hug 1999; Christensen et al. 2000). Microorganisms can reduce Cr(VI) in soil by both direct and indirect mechanisms. Indirect microbial chromium reduction proceeds through depletion of oxygen, reduction of Fe and S (Lovley et al. 1991; Chapelle 1992), and production of organic ligands and reductants. Direct microbial enzymatic reduction of Cr(VI) in soils has also been reported (Lovely 1993; Losi et al. 1994a, 1994b; Chen and Hao 1998). A comparison of abiotic versus enzymatic Cr(VI) reduction kinetics indicates that the abiotic pathways are expected to be dominant in most soils under reducing conditions (Fendorf et al. 2000). Nonetheless, soil biological influences are expected to remain dominant, through promoting the indirectly microbial chromium reduction processes mentioned above.

Using microbial studies of sediments collected at the Hanford 100H site, we determined the presence of several types of bacteria, including *Bacillus/Arthrobacter and Geobacter* species. These bacteria are known to withstand high concentrations of heavy metals (Margesin and Schinner 1996), metabolize recalcitrant chlorinated compounds (Edgehill 1996) and reduce or sorb hexavalent chromium (Megharaj et al. 2003; Quintelas and Tavares 2001). Metal reducing bacteria could contribute to Cr(VI) bioreduction either indirectly or directly. Cr(VI) bioreduction could occur along with chromium reduction by Fe(II) (Fendorf et al. 2000).

Phospholipid fatty acid analyses (PLFA), terminal restriction fragment length polymorphisms (TRFLP), clone libraries, direct cell counts, and 16s rDNA microarray analysis demonstrated that the initial densities of microbes is very low ($<10^4$ cells/g), but after biostimulation increased typically to more than 10^8 cells/g. The low densities of microbial communities made extraction for PLFA and DNA analysis difficult, so a cell concentration technique was developed to increase yields. These studies confirmed that the microbial diversity was low, but that sulfate reducers, *Arthrobacter* spp. and *Geobacter* spp. dominated the samples.

In a series of laboratory tests conducted at LBNL, ^{13}C-labeled lactate was added as a bioreactive tracer for examining the relationship between utilization of lactate and Cr-reduction in the treatability studies. In these experiments, the carbon isotope ratios of dissolved inorganic carbon (DIC) in the solutions were shifted to higher ratios, approximately tracking the levels of Cr-reduction that were observed. In our experiments, the ^{13}C values shifted considerably—up 100 permil, while a detection limit is ~0.5 permil. (Similar measurements will be made during the field experiments to monitor subsurface microbial activity—see Research Plan, Subtask 1.2).

The results of LBNL experiments demonstrate that even in a low biomass and diversity environment biostimulation of Cr-reducers can occur and that their functional relationship can be evaluated by various molecular techniques. Note that decreases in Cr(VI) (aq) do not prove precipitation of Cr(III), since Cr(VI) sorption may also be involved, especially if addition of carbon causes the system pH to decrease. The test results also indicate that the reduction in Cr(VI) was mainly caused by biological activity, while the abiotic reduction was not significant. However, because Cr(VI) reduction in sediments is diffusion rate-limited, a small fraction of Cr(VI) could remain unreduced and continue moving with the regional flow. In addition, the presence of manganese minerals and dissolved oxygen could cause a small portion of Cr(III) to reoxidize to Cr(VI). These studies suggest that understanding of hydraulic, geochemical, and microbial conditions necessary for maintaining complete bioreduction of Cr(VI) and a long-term stability of Cr(III) in soils is essential for designing effective strategies for reducing environmental risk. These studies along with field studies in progress will be used to develop a conceptual model of chromium bioreduction in groundwater at a field scale and to provide recommendations for field deployment of lactate-stimulated bioremediation.

A.3   Polylactate Bioreduction Technology

The polylactate compound offers a passive, low-cost treatment technology for *in situ* anaerobic bioremediation of chlorinated hydrocarbons and metals (Koenigsberg 1999). The polylactate compound is an environmentally safe, food quality, polylactate ester specially formulated for the slow release of lactic acid upon hydration. The polylactate compound is manufactured as a dense (density of 1.3 g/cm^3) and viscous gel (viscosity of approximately 20,000 centipose), containing the slow and fast releasing polylactate esters. The slow releasing compound is bound in a highly viscous polymer that releases the lactic acid slowly. The fast releasing compound is bound in a low viscous polymer that releases the lactic acid fast (up to one order of magnitude faster than the slow release compound) and can affect a larger volume of water. Indigenous anaerobic microorganisms ferment lactic acid or lactate to produce hydrogen (H_2) that is a required electron donor for reducing Cr(VI), dissolved in groundwater, to Cr(III) that is then precipitated onto sediment particles.

The polylactate compound,upon hydration, releases lactic acid, providing carbon and energy sources for both aerobic and anaerobic microbes, thus enhancing redox conditions and microbial populations. Lactic acid then degrades into pyruvic acid followed by acetic acid, releasing CO_2 and 2 moles of molecular hydrogen per mole of lactate (Figure A.6.). Hydrogen is a primary electron donor to reduce electron acceptors, such as oxygen, nitrate, iron, and sulfate.

As a result, the redox potential and dissolved oxygen drop to zero, creating the conditions for transforming Cr(VI) species to chrome Cr(III) species that are then precipitated on soil particle surfaces.
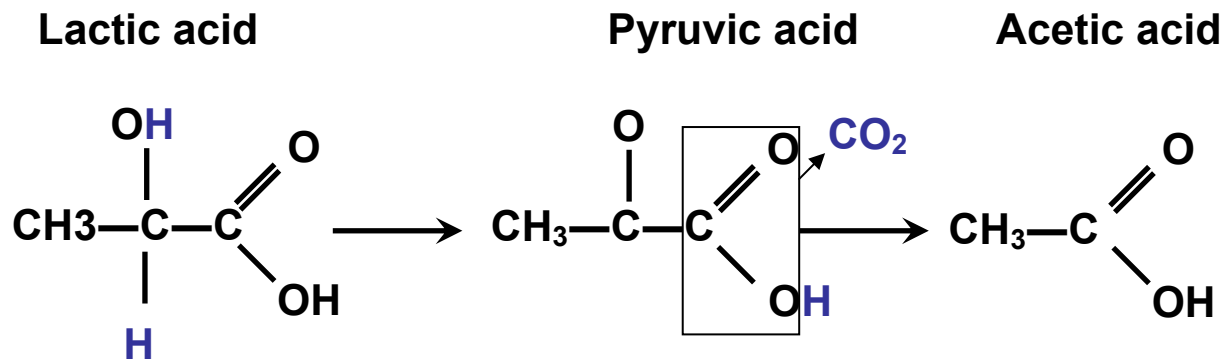
Lactic acid   **Pyruvic acid**   **Acetic acid**

Figure A.6. A schematic showing lactic acid degradation into pyruvic acid followed by acetic acid, releasing CO2 and hydrogen.

A.4 Need for Chromium Immobilization Upgradient from ISRM

In 1999, the 100-HR-3 ROD (1996) was amended to address remediation of a newly discovered chromium plume in the southwestern portion of the 100-D Area. This plume and the larger one northeast of it contain the highest chromium concentrations in the groundwater (>2000 ppb) on the Hanford Site, as well as the highest concentration of chromium in the aquifer sampling tubes (e.g., >200 ppb) installed on the river shore. This area is located adjacent to major salmon spawning beds in the Columbia River. The ROD Amendment calls for deployment of the In Situ Redox Manipulation (ISRM) technology, a permeable reactive barrier that reduces chromium from the hexavalent form to the immobile and less toxic trivalent form. This technology was tested and evaluated for several years in the 100-H area prior to deployment in the 100-D Area. The main purpose of the ISRM barrier is to protect the salmon beds by reducing chromium levels to below the aquatic standard of 10 ppb. The 680 m ISRM barrier was installed in three phases, from 1998 to 2002.

It is clear from monitoring data that this plume is being fed by a continuing source of hexavalent chromium. Locating and remediating this source is a high priority task for the Groundwater Remediation Project, but even after source remediation the 700 m-long plume will continue to be a threat to the river. Current modeling predicts it will take at least 40 years for the plume with concentrations > 20 ppb to move through the ISRM barrier, which is well in excess of the 20-year design life of the barrier.

Although the primary purpose of the ISRM was to immediately protect the Columbia River, additional cleanup is required to address the high concentration portion of the chromium plume behind the ISRM and to increase the longevity of the barrier, portions of which have been exhibiting signs of premature breakdown. The proposed method to accomplish this is to introduce polylacte into the aquifer to bioreduce hexavalent chromium and establish a permeable reactive barrier that will continue to treat chromium under natural groundwater flow conditions.

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Appendix B

Response to Summary Comments from Supplemental Columbia River Activities Peer Review

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Responses to Supplemental Columbia River Protection Activities Peer Review

Proposal Title: **Initial Calcium Polysulfide Test for Accelerated Clean Up of the Southwestern Chromium Plume in the 100-D Area**

STATEMENT REGARDING RESPONSES: The revised proposal details the change in direction from deploying calcium polysulfide to utilizing bioremediation. The following responses to comments address some aspects of the original scope, but in some instances may not provide a complete answer because of the decision to deploy a different remediation technology.

Technical Basis of the Proposal:

The panel believes a proposal to chemically reduce Cr(VI) to Cr(III), as well as the flux of other oxidants to the ISRM barrier, is based on valid and appropriate science, and fits well with the integrated systems approach to accelerate the cleanup of Cr(VI) contamination near the Columbia River. Such a strategy supports a "defense in depth" environmental management strategy, which was recommended by the National Academy of Sciences and the National Research Council. Use of CPS to achieve this goal is potentially viable, but the panel believes that alternative reductants and electron donors are likely to be better choices – i.e., less aggressive and toxic when applied and providing a longer period of chromium conversion and oxygen and nitrate scavenging.

General Technical Issues for Consideration:

1. The proposal did not adequately describe where the injections would take place, at what depth, and in what ways one would expect CPS to be better than alternatives – the selection of CPS was not justified. An alternatives analysis that is linked to the 100-D Area conceptual model and linked to the 100-D Area systems approach for protecting the Columbia River is required to move this strategy forward. (see reviewers 2, 4, 5, 6, 7, and 8)

   Response: Agree. The revision will address these concerns.

2. Demonstrate how the proposed number of injection wells was determined and if it is appropriate.

   Response: Agree. This will be addressed in the revision.

3. Consider the impacts of subsurface heterogeneity on the delivery and transport of CPS. The proposal does not provide an adequate explanation for how CPS will be delivered.

   Response: Agree.

4. Consider the impacts of CPS toxicity and other geochemical interactions on the aquifer geochemistry and microbial populations therein. Also, the impacts of the byproduct formation

and increase in pH on the downgradient Columbia River should be considered – there is a need to balance the potential impacts of higher pH and other perturbed chemistry versus ppb levels of Cr(VI) on salmon breeding zones. (see reviewers 1, 3, 7, and 8)

Response: Agree. Several of these concerns can be (and have been) evaluated based on results from the CPS treatability test that was performed at the 100-K area in 2005. There were short-term increases in metal mobility, but levels decreased to near normal after a few months. pH in the injection wells has decreased from approximately 10.4 to 9.7, and is as low as 8.8 in one well (background is about 8.0). In the extraction well pH rose to over 9 but returned to background about a month after the test concluded.

5. CPS and zero-valent iron (ZVI) are not compatible, so injecting CPS too closely to the ISRM barrier could impact its effectiveness. (see reviewer 2)

   Response: Agree.

6. Address the impacts of CPS on the geochemistry of the subsurface, groundwater, and river (see reviewers 1, 2, 3, 6, 7, and 8):

   – CPS could release significant amounts of sulfur in the subsurface that could be oxidized by soil bacteria to form sulfuric acid, which lowers soil pH. Given the potential of the ISRM barrier to raise pH, this acidification may be beneficial overall, but the potential long-term effects of adding large amounts of sulfur to the aquifer should be carefully considered. Also, the possibility of CPS to produce sulfate could impact the effectiveness of the downgradient ISRM barrier and the proposed electrocoagulation treatment system for the proposed expansion of the pump and treat system by plugging pores.

     Response: Agree. If CPS is deployed it would be situated so as not to impact the barrier and/or pump & treat system.

   – Consider the impacts of introducing a significant amount of calcium into a system that may be naturally saturated with calcite.

     Response: This was considered and evaluated in the treatability test. Significant precipitation of calcite would decrease the saturated hydraulic conductivity of the formation; pre- and post-treatment slug tests show that permeability actually increased slightly after the test.

   – Safety, process, and handling issues need to be better considered for CPS. For example, CPS reacts explosively with strong acid to form hydrogen sulfide.

     Response: Agree. No strong acids would be present at the site.

   – CPS could cause the mobilization of naturally occurring arsenic and other trace **elements.**

     Response: This continues to be evaluated at the treatability test.

   – The high pH of CPS could disperse clays and initially mobilize chromate.

Response: The formation is essentially devoid of clays.

– The high pH and low Eh of CPS will alter the aquifer geochemistry – the effects of shifts in these controlling "master variables" on the major and trace elements, including contaminants, should be generally evaluated.

Response: The treatability test addressed this issue, and did not find any long-term impacts on aquifer geochemistry beyond redox conditions**.**

– Consider the quality of the groundwater after treatment and its compatibility with the downgradient ISRM barrier.

Response: Agree.

7. Address the concern that using this technology to create an upgradient treatment zone is somewhat redundant with the ISRM barrier, if the same objectives are set for each process. The upgradient treatment objectives need to be set to be consistent with the role of the process in the overall systems approach.   The upgradient treatment could be targeted to reduce oxygen and nitrate in the groundwater, so that when the groundwater reaches the ISRM barrier, treatment can focus on reduction of chromate.

Response: An upgradient technology that treated the entire plume would be redundant with ISRM. The concept is to treat the portion of the plume that is highest in chromate. A technology that reduces in situ reduction technology (i.e., addition of iron or calcium polysulfide, or bioremediation) should reduce or eliminate nitrate, dissolved oxygen, and hexavalent chromium.

8. It might be more appropriate to use CPS to address the contamination source or areas of high contamination, rather than to be deployed broadly across a dispersed plume. It might be "too big a hammer" to use for existing concentrations of chromium. Evaluate less aggressive, more benign reductant alternatives.

Response: Agree.

9. Consider that CPS is a relatively new technology that has not been well tested.

Response: CPS has been successfully used for chromate remediation in several areas in the U.S. and abroad for both groundwater and vadose zone remediation. It has also been successfully tested at Hanford.

10. Evaluate alternatives to CPS using a consistent unit for comparison (e.g., based on electron donor potential and the profile of the impacts through time). Reductant alternatives to CPS include (see reviewers 1, 2, 4, 5, 6, 7, and 8):

– Various organic reductants (e.g., lactate, carbohydrates like molasses or corn syrup, vegetable oil or emulsified vegetable oil, proprietary products like HRC Advanced, etc.) with potential to remove chromate from the groundwater. In addition to removing chromate, organic reductant would also remove oxygen and nitrate, reduce the amount of precipitated sulfur, and be safer and significantly cheaper than CPS.

Response: Agree. The revised proposal has switched the remediation agent from CPS to organic reduction. There are several reasons for doing this:

○ Sulfur produced from CPS reaction could negatively impact the ISRM barrier

○ Agreement that CPS could be too aggressive for the relatively small concentrations of chromate in the groundwater

○ It will have a far smaller effect on the geochemistry of the aquifer

– Inorganic reductants (e.g., iron sulfates, sodium dithionite, etc.)

– A combination of organic nutrient reductant and CPS.

Response: See previous response.

11. Consider pump and treat.

Response: The Site strategy is to continue to treat this plume passively. Installation, operation, and maintenance expense of a P&T system is a concern. The fact that this plume has a continuous source which has yet to be discovered is also an appealing reason to address contamination with a persistent remediation technology.

Implementation Strategy:

12. The panel generally supports the proposed sequencing and timing. Implementing reductant injection should be strongly coordinated with the other projects in the integrated systems approach.

Response: Agree.

13. Injecting an upgradient treatment might be better delayed until results of the ISRM barrier mending with ZVI are complete and the alternatives evaluation is completed and peer reviewed.

Response: The proposed location for treatment will be significantly upgradient from the ISRM so that treated groundwater should not reach the barrier for several years. This will allow enough time for evaluation of ZVI injection.

14. Consider a dipole deployment (i.e., a combination of injection and extraction).

Response: Agree.

15. The proposal provides little description of costs associated with implementation, such as the location of wells, operating costs, etc. A significant portion of the project is allocated for installation of wells. Consider alternatives. Infiltration galleries should be considered as an alternative.

Response: The revised proposal contains much greater detail on well locations and the necessity for direct aquifer injection.

16. The proposal should include a more detailed discussion of budget costs. Consider the relatively high costs of applying CPS over a large area.

    Response: Agree.

17. Consider orienting the treatment parallel to flow, through the middle of the plume to treat as much chromium as possible. (This concept would need to be performed as an injection/extraction system to avoid spreading the plume.)

    Response: This strategy would treat a greater mass of chromate but would not have a widespread effect on the ISRM barrier.

18. Consider potential stakeholder concern that this technology does not address the source of chromium contamination. Stakeholders might be more amenable to using CPS if the source of chromium contamination were known and the highest concentrations were targeted with such an aggressive reagent.

    Response: Comment noted.

19. Consider that injecting CPS may be too aggressive as an upgradient treatment to augment the ISRM barrier. The ISRM barrier, which is proposed for mending, provides an effective treatment and the reductant should be designed to be cost effective and safe while recognizing that the action is part of the systems approach.

    Response: Agree.

20. The proposal needs to provide a better and more detailed description of the pilot field test; however, a pilot test may not be necessary considering one was completed in the Hanford 100-K Area.

    Response: Comment noted.